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# Evolution of crystallinity of GaN layers grown at low temperature on sapphire with dimethylhydrazine and triethylgallium

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## Abstract

The crystallinity of GaN layers grown at low temperature by organometallic vapor phase epitaxy on sapphire using dimethylhydrazine and triethylgallium has been studied with Raman spectroscopy, atomic force microscopy and Rutherford backscattering spectroscopy. The layers were grown in the temperature range from 520°C to 660°C. Amorphous, possibly non-stoichiometric Ga-rich layers were produced below 560°C. Smooth layers of crystalline GaN with a disordered structure were produced between 560°C and 600°C. Rough but crystalline layers were produced at higher temperatures. The minimum temperature for production of crystalline layers occurs at about 580°C. © 2001 Published by Elsevier Science B.V.

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## 1. Introduction

Gallium nitride (GaN) has a large, direct bandgap and is used, in combination with its alloys with aluminum and indium, in the fabrication of short-wavelength light-emitting diodes and lasers [1,2]. A number of other electronic devices for high power switches and

microwave power amplification are being developed [3,4]. Organometallic vapor phase epitaxy (OMVPE) on sapphire substrates using ammonia and trimethyl (or triethyl) gallium is the most prevalent deposition method [2]. The technique is widely used and well documented. Growth is carried out at 1000°C and above. GaN alloy containing In are less stable at high temperature and could benefit from the use of a low temperature process. In that regard, dimethylhydrazine (DMHz) is an attractive N source because it has a lower decomposition temperature (50% decomposition occurs at  $D_{50}=550^{\circ}\text{C}$ ) than ammonia,

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which is only 30% decomposed at 900°C [5,6]. Therefore it could, in principle, allow growth of nitride alloys at relatively low temperatures. Dimethylhydrazine, however, has already been used successfully as a liquid phase nitrogen precursor for growth of the cubic phase of GaN on GaAs [7,8], for growth of alloys (GaInAs) at low temperatures [9,10] and for growth of GaN on sapphire [11].

Growing GaN by OMVPE using dimethylhydrazine instead of ammonia, we found strong similarities with growth of GaN using ammonia in terms of growth scheme and temperatures [12]. In particular, we obtained smooth epitaxial layer from a two dimensional growth mode at high temperature ( $>990^{\circ}\text{C}$ ). We found that GaN can be grown at lower temperature but growth proceeds in three dimensions which results in rough surfaces. This is also observed for growth with ammonia. However, contrary to growth with ammonia, GaN epitaxial film can be grown on either thin or very thick (up to 150 nm) low-temperature buffer layers. Successful growth of GaN on sapphire using ammonia has only been achieved by using a thin buffer layer (about 25 nm) grown at low temperature which provide a nucleation layer for subsequent epitaxy at higher temperature. GaN [13], AlN [14] and InN [15] buffer layers are being used. It is well known that the characteristics of these low-temperature buffer layers have a large effect on the quality of subsequent gallium nitride film growth and on the performance of the resultant device (see, for example, Refs. [16–19]).

This paper attempts to answer two questions: (1) at what temperature can crystalline GaN be obtained with DMHz and (2) is the structure of these low-temperature layers different from that of the low-temperature layers grown with ammonia? To that purpose, we have investigated the structure of low-temperature layers grown with DMHz vs. deposition temperature and attempted to compare them to the structure of buffer layers grown with ammonia. Low-temperature layers were grown at temperatures above and below  $D_{50}$ . Their structure was evaluated with Raman spectroscopy, atomic force microscopy (AFM), and Rutherford back-scattering spectrometry (RBS).

## 2. Experimental procedure

The GaN samples were grown by organometallic vapor phase epitaxy (OMVPE) on sapphire (0001) in a low-pressure vertical, cylindrical stainless-steel reactor equipped with a radiatively heated high speed rotating wafer carrier. The precursors to GaN were triethylgallium (TEGa) and dimethylhydrazine (DMHz). Pd-purified hydrogen was used as the carrier gas. The layers were grown at a pressure of 60 Torr and a V/III molar flow ratio of 55. Prior to growth, the sapphire substrates were cleaned in situ in a flow of hydrogen at a temperature of 1050°C for 10 min. Dimethylhydrazine was used for nitridation of the substrate at 1000°C. Triethylgallium was introduced at the nucleation temperature which was varied from 540°C to 660°C. The resulting layers were rapidly cooled and removed from the growth chamber without subsequent epilayer growth.

An argon ion laser emitting at 488 nm was used as exciting light source for the macro-Raman measurements. All Raman spectra were recorded at room temperature in air in the back-scattering configuration. The incident laser power was 50 mW and the instrumental resolution was about  $1\text{ cm}^{-1}$ .

## 3. Results and discussion

Six low-temperature layers were produced and their thicknesses were determined by Rutherford backscattering spectrometry (RBS). They are listed in Table 1. At 540°C, the growth rate was  $2.4\text{ nm min}^{-1}$ . It stayed approximately constant at  $3\text{ nm min}^{-1}$  from 560°C to 640°C.

Fig. 1 shows the Raman spectrum of the low temperature layers. The position of the  $E_2$  mode of crystalline GaN is indicated for reference. The prominent peak from the buffer layers grown at 580°C and higher is the broadened LO phonon. A weak peak at  $578\text{ cm}^{-1}$  comes from the sapphire substrate. The GaN  $E_2$  peak is not seen in these spectra. These spectra also contain a broad feature around  $660\text{ cm}^{-1}$  and a weaker feature at  $600\text{ cm}^{-1}$ . The peak at  $660\text{ cm}^{-1}$  has been observed before in disordered material produced by ion

Table 1

Thickness of buffer layers chosen for the Raman spectra shown in Fig. 1

Buffer layer temperature (°C)	Thickness (nm)
540	145
560	185
580	205
600	180
620	185
640	220
660	185

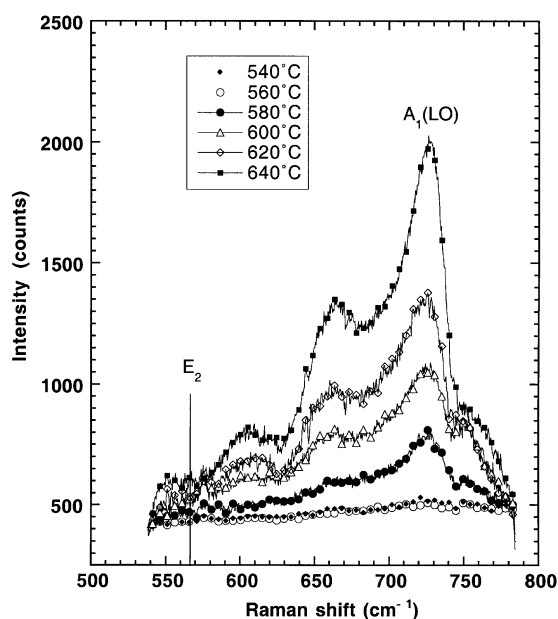


Fig. 1. Raman spectra of thick buffer layers grown at temperatures between 540°C and 640°C.

implantation [20], in materials subjected to high temperature annealing [21] and, in general, in non-intentionally doped n-type GaN [22]. The peak at  $600\text{ cm}^{-1}$  was seen in high-temperature annealed material as well [21]. Both peaks correspond to features in the phonon density of states [23] and are observed here in Raman scattering due to selection rule breakdown stemming from disorder in the film. Therefore, we conclude that these films are crystalline but disordered. These buffer layers may also contain a large density of the defects

responsible for the unintentional n-type doping [24]. No peaks were observed in the Raman spectra of the buffer layers grown at 540°C and 560°C although RBS clearly indicates that a film is present. This indicates that films grown at these temperatures are amorphous, non-crystalline and, possibly, Ga-rich and therefore would not be expected to have strongly featured Raman spectra. The layers grown below 560°C have a very pale-grayish color that would also indicate a lack of stoichiometry and the presence of an excess of Ga also seen in the RBS spectra.

These observations are quite different from results obtained by Demangeot et al. [25] for growth of buffer layers with ammonia. In their study, the  $E_2$  mode appears in buffer layers grown above 550°C, indicating that using ammonia as a precursor appears to make a more ordered buffer layer at these temperatures. However, we must note that the temperature measurements in an OMVPE reactor can vary substantially from one reactor to the other. We measured sample temperatures with a thermocouple located just under the substrate carrier. The top surface of the sapphire substrate is believed to be slightly colder than the recorded temperature.

The buffer morphology was evaluated with AFM (Fig. 2). The layers grown below 580°C appear smooth. At 580°C small hillocks are observed. The roughness of the buffer layers increases with temperature. At 640°C and above, well defined hexagonal GaN pyramids form. At this temperature the buffer layer is no longer continuous but clearly crystalline. These morphology findings correlate well with the Raman results.

As mentioned previously, we found that using DMHz and TEGa, the morphology of the high temperature grown epitaxial layers is much less affected by the thickness of the buffer layer than it is when growth is carried out with ammonia. Low-temperature layers of thickness varying between 15 and 150 nm have been used as buffer layers prior to growth of the high-temperature GaN epitaxial layer. Contrary to what is observed for growth with ammonia [2], the morphology of the high temperature epitaxial layer is not affected by the thickness of the buffer layer. The dislocations density revealed by TEM images in the resulting

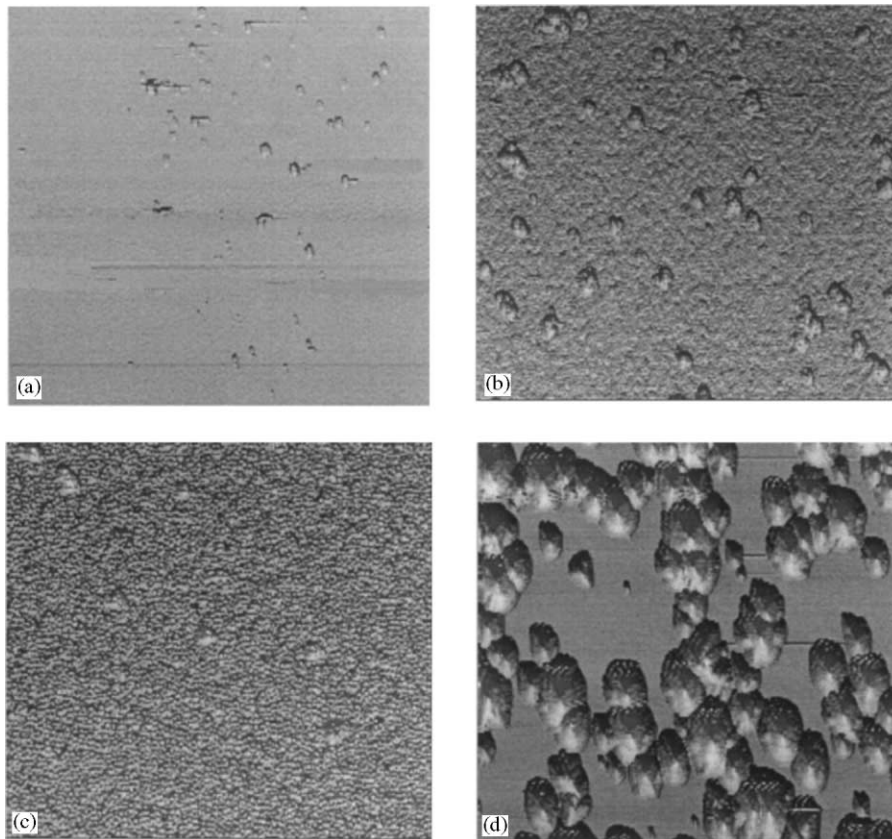


Fig. 2. AFM images showing the morphology of buffer layers on a  $5\mu\text{m} \times 5\mu\text{m}$  area: (a) layer grown at  $580^\circ\text{C}$ , 40 nm thick (b) layer grown at  $600^\circ\text{C}$ , 50 nm thick (c) layer grown at  $620^\circ\text{C}$ , 37 nm thick (d) layer grown at  $640^\circ\text{C}$ .

epitaxial layer is about  $4 \times 10^9 \text{ cm}^{-2}$  which is similar to the dislocation density of layers grown with ammonia. Raman and RBS (in the  $\langle 0001 \rangle$  channeling orientation) measurements also revealed no major differences between films grown with buffer layer temperatures in the  $560\text{--}600^\circ\text{C}$  range. The near surface minimum yield,  $\chi_{\text{min}}$  (defined as the ratio of the spectrum obtained in the channeled orientation to that in a random direction) was 1.5% for these films, indicating high-quality epitaxial layers. In the Raman spectra, we could detect small stress-induced changes in the position of the  $E_2$  peak. When converted to stress using the method described in Ref. [16], we find that a buffer layer grown at a temperature of  $580^\circ\text{C}$  produces the minimum compressive residual stress in the film (Fig. 3). For buffer layer

temperatures below  $560^\circ\text{C}$  and above  $600^\circ\text{C}$ , only very poor quality GaN films were obtained. This implies that the non-crystalline and most likely non-stoichiometric GaN layers formed below  $560^\circ\text{C}$  and the crystalline but discontinuous and rough layers formed above  $600^\circ\text{C}$  are poor buffer layers for subsequent GaN growth. This leads us to hypothesize that the stoichiometry of the low-temperature layers is a major parameter to promote subsequent growth of GaN. It appears that if a continuous and not Ga-rich layer is produced, then its thickness is of lesser importance. These results are consistent with the results of Kim et al. [26] who show that for MBE growth the buffer layer composition controls the material properties. In their study they demonstrate that for very thin buffer layers (only 4 nm), a Ga-rich

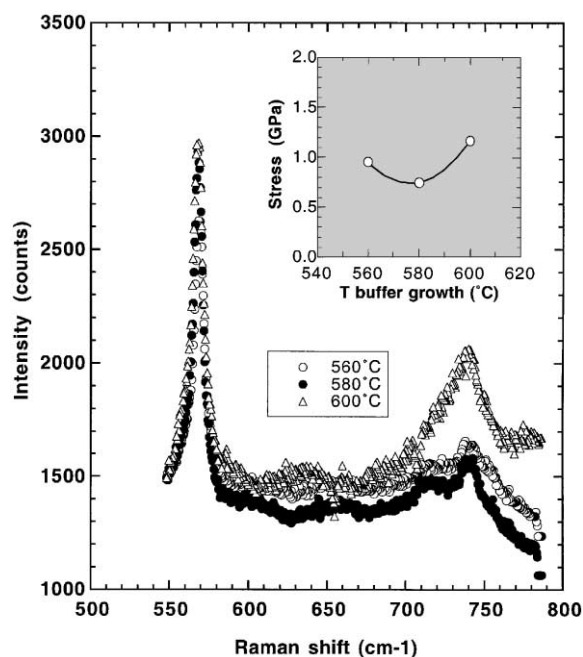


Fig. 3. Raman spectra of GaN epilayers grown at 1000°C on thick (about 150 nm) low temperature layers grown at various temperatures. Inset shows residual compressive stress calculated from the shift of the  $E_2$  phonon with respect to a stress-free single crystal.

buffer layer promotes growth of better material because such a Ga-rich layer can relieve the stress at the growth temperature. This highly non-stoichiometric layer must be very thin to be mainly a wetting layer, while a smooth stoichiometric layer can be thicker.

#### 4. Summary

In summary, we have grown low temperature GaN layers at low temperature using dimethylhydrazine and triethylgallium. Characterization using Raman scattering, atomic force microscopy and Rutherford backscattering shows that disordered, but crystalline GaN layers are obtained in the temperature range 560–600°C. Amorphous, non-crystalline, possibly non-stoichiometric Ga-rich layers were produced below 560°C. Rough but crystalline layers were produced

at higher temperatures. The minimum temperature for production of crystalline layers occurs at about 580°C.

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